08/795961 PTO

02/04/97

MAIL ROOM FEB 4 1997 PAT. & TRADEMARK OFF.

The Patent Office

#2

The Patent Office
Cardiff Road
Newport
Gwent
NP9 1RH

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation and Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.

Signed

Dated 24 OCT 1996

Patents Act 1977
(Rule 16)

The Patent Office

01FEB96 E171277-1 D00013
F01/7700 25.00

THE PATENT OFFICE
G
31 JAN 1996
RECEIVED BY POST

The Patent Office
Cardiff Road
Newport
Gwent NP9 1RH

Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

1. Your reference — 9935/04

2. Patent application number *(The Patent Office will fill in this part)* — 31 JAN 1996 — **9601915.3**

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

   KODAK LIMITED
   PATENTS
   HEADSTONE DRIVE
   HARROW, MIDDLESEX. HA1 4TY

   Patents ADP number *(if you know it)*

   If the applicant is a corporate body, give the country/state of its incorporation — UNITED KINGDOM

   10240016

4. Title of the invention

   METHOD OF TREATING WASTE EFFLUENT

5. Name of your agent *(if you have one)*

   "Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

   P A C BARON

   KODAK LIMITED
   PATENTS
   HEADSTONE DRIVE
   HARROW, MIDDLESEX. HA1 4TY

   Patents ADP number *(if you know it)* — 26443002

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing *(day / month / year)*

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:*
   a) any applicant named in part 3 is not an inventor, or
   b) there is an inventor who is not named as an applicant, or
   c) any named applicant is a corporate body.
   See note (d))

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form	
Description	12
Claim*(s)*	3
Abstract	1
Drawing*(s)*	5

10. If you are also filing any of the following, state how many against each item.

Priority documents	
Translations of priority documents	
Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	
Request for preliminary examination and search *(Patents Form 9/77)*	
Request for substantive examination *(Patents Form 10/77)*	
Any other documents *(please specify)*	

11. I/We request the grant of a patent on the basis of this application.

Signature H C Haile Date 30.01.96

12. Name and daytime telephone number of person to contact in the United Kingdom H C HAILE 0181 424 4419

Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

Notes

a) *If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505.*

b) *Write your answers in capital letters using black ink or you may type them.*

c) *If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.*

d) *If you have answered 'Yes' Patents Form 7/77 will need to be filed.*

e) *Once you have filled in the form you must remember to sign and date it.*

f) *For details of the fee and ways to pay please contact the Patent Office.*

METHOD OF TREATING WASTE EFFLUENT

Field of the Invention

The present invention relates to a method of treating waste effluent, in particular photographic effluent, which contain reduced species, especially sulphur-oxygen species, such as, for example, thiosulphate or sulphite. The present invention also embraces apparatus for performing such methods of treatment.

Background of the Invention

It is usual for photographic effluent for both black-and-white and colour processing to contain one or more reduced sulphur-oxygen species. Thiosulphate or "hypo" is commonly used as a fixing agent, and sulphite ions are often included in developer solutions and/or stop/clearing baths as a preservative scavenger for oxidised developing agent. Sulphite is also known as a fixing agent. DE-A-3635219 to AGFA-GEVAERT AG discloses treating dilute aqueous solutions of thiosulphate by oxidation with hydrogen peroxide in the presence of a chromium, vanadium, tungsten or molybdenum compound as catalyst and discloses that molybdate is preferred. It is desirable to oxidise thiosulphate in photographic effluent before discharging the effluents to a sewage system, in order to reduce the chemical oxygen demand (COD) of the effluent.

Problem to be Solved by the Invention

A problem with the treatment method disclosed by DE-A-3635219 is that, while the COD of the thiosulphate-containing photographic effluent is reduced, transition metal contaminants are added to the effluent as catalyst which are subsequently discharged

into the environment. This is clearly undesirable for environmental reasons, and is also an inefficient use of the transition metals. It is an object of the present invention to provide an improved treatment method for waste effluent, and in particular photographic effluent, containing reduced species, which does not involve the discharge of transition metal species to the environment and in which the transition metal species can be reused.

Summary of the Invention

According to one aspect of the present invention therefore there is provided a method of treating waste effluent containing reduced species, by oxidation with hydrogen peroxide, or a compound capable of releasing hydrogen peroxide, in the presence of a catalyst therefor, characterised in that said catalyst is immobilised on a substrate therefor.

The reduced species may generally be a sulphur-oxygen species, typically as thiosulphate or sulphite.

Said catalyst may be selected from molybdate, tungstate, chromate and vanadate, although molybdate and tungstate are particularly preferred.

Typically the substrate will constitute a porous mass which permits permeation of the photographic effluent into its interstices, thereby presenting a large surface area of catalyst to the effluent. Said substrate may be anionic, and in a particular aspect of the present invention the substrate comprises an anion exchange material. In some embodiments, a

mixture of anion and cation exchange materials may be used. The material may typically be a polymeric resin or clay or zeolite-type material.

In another aspect, the present invention contemplates a photographic development process in which effluent from one or more of the development steps are treated continuously or batch-wise by the method according to the present invention. Usually, the effluent from each stage will be combined and treated together. Said development process may be an RX process which is performed upon a photographic element containing a reduced silver lay-down density as compared with conventional silver halide photographic materials. As will be well known to a person skilled in the art, hydrogen peroxide is employed in the development step of an RX process, in which case it may be unnecessary to add additional peroxide to the photographic effluent. Of course, additional peroxide may be added to the effluent if required.

Compounds capable of releasing hydrogen peroxide include metal peroxides; compounds which include hydrogen peroxide in their crystal structure such as sodium percarbonate; other peroxy compounds such as sodium perborate and persulphate; or soluble organic peroxide, such as butyl peroxide or benzyl peroxide. The peroxide is added in an amount sufficient to cause oxidation of a substantial proportion of the reduced species and is conveniently hydrogen peroxide itself.

Where the photographic effluent is treated batch-wise, the catalyst may be disposed within a receptacle which is equipped with an inlet for introducing photographic

effluent from the development process and an outlet for discharging treated effluent to waste. The outlet will be fitted with selectively operable closing means for closing the outlet during conduction of the treatment method, typically a valve.

Alternatively, the treatment method may be performed continuously on effluent delivered from the photographic development process. In another aspect of the present invention therefore the catalyst/substrate may be packed in a conduit which is arranged to receive photographic effluent in one end, and to deliver the treated photographic effluent from the other end. The flow rate of photographic effluent through the conduit will be adjusted such that the average residence time of effluent within the conduit is sufficient to oxidise a substantial proportion of the reduced sulphur-oxygen species contained in the effluent.

Where thiosulphate-containing effluents from the fixing stage are treated in accordance with the present invention, silver that has been complexed during fixing may be precipitated in the treatment stage. In some embodiments therefore silver-bearing precipitate may be separated from the treated photographic effluent before the effluent is discharged. For this, filtering or centrifuging means may be employed.

Advantageous Effect of the Invention

According to the present invention therefore a method of treating waste effluent containing reduced species, preferably containing sulphur-oxygen species, is provided which does not involve discharging transition metal species into a sewage system. This is advantageous from the environmental perspective, and also means that the transition metal catalysts can be reused which is more efficient in these materials as compared with the prior art processes. Unexpectedly, the present applicants have found that by supporting the transition metal catalysts on a substrate therefor, substantially less catalyst can be used as compared with the prior art processes without impairing the efficiency of the treatment reaction. For example, the treatment method of the present invention can be performed effectively using less than 1/100 parts by weight catalyst, and typically less than 1/250 parts by weight of sulphur-oxygen species. It was also found surprisingly that use of a supported catalyst in accordance with the present invention appeared to cause or allow more complete destruction of sulphur-oxygen species to sulphate as compared with prior art processes using unsupported catalyst.

Brief Description of the Drawings

Figures 1 to 4 of the accompanying drawings are graphs of pH verses time for reactions of photographic effluent with peroxide in the presence of a supported catalyst as detailed in the following specific description.

Figure 5 shows the holding tank for performing the treatment method of the present invention.

Figure 6 shows a conduit in accordance with the present invention for performing the treatment method.

The invention will now be described with reference to the following Examples which are not to be construed as limiting in any way.

Detailed Description of the Invention

EXAMPLE 1

A "mock" effluent from a low silver RX colour process was made up from the following solutions:

Developer:

1-hydroxyethylidene-1,1'--diphosphonic acid	0.6g
Diethyltriaminepentaacetic acid	2.0g
Dipotassium hydrogen phosphate	40.0g
Hydroxylamine sulphate	0.5g
CD3	4.5g
Hydrogen Peroxide (30%)	2ml
Water to	1 litre
pH adjusted to 11.7	

[CD3 = 4-amino-3-methyl-N-ethyl-(2-methanesulfonamido-ethyl)aniline sesquisulfate hydrate.]

A pseudo seasoned fix/stop was made up with the following constitution:

Sodium thiosulphate pentahydrate	20g
Sodium meta bisulphite	30g
Sodium acetate	40g
Silver chloride	1.2g
Water to	1 litre

The pH of the fix/stop measured at 25C was adjusted to

6.3 with sodium hydroxide.

Effluent = 6 parts developer + 5 parts fix/stop + 20 parts water.

Molybdate ions were first adsorbed on an anionic resin using the following method. 10g of Amberlite® IRA-400 exchange resin (manufactured by Rohm and Haas) was stirred gently in 50ml demineralised water. To this was added 2ml 1% ammonium molybdate solution. This mixture was stirred for 10 minutes and then the liquid was decanted from the resin and the resin was washed with 3 x 50ml changes of demineralised water. The drain resin was used for the following experiments.

100ml of effluent at room temperature (22C) were placed in a 150ml beaker on a magnetic stirrer and stirred gently. A glass pH electrode and calomel reference electrode were placed in the solution and connected to a Radiometer pH meter, the meter having being calibrated previously with reference pH buffers. The pH was recorded. 30ml of 3% hydrogen peroxide were quickly added and the pH was recorded after 10sec and then as felt appropriate until the pH stayed constant. At the end of the run the treated liquid was removed and analyzed for molybdenum by atomic adsorption spectroscopy. To demonstrate the invention the experiment was repeated with the 10g treated resin added. At the end of the run the resin was filtered off before the treated liquid was sent for molybdenum analysis as before. The experiment was again repeated but this time with 2ml 1% ammonium molybdate added directly to the mixture of effluent and peroxide with no resin present.

The levels of molybdenum in the treated effluent are shown in the following table:

Effluent treatment	Mo in Final Effluent ppm
Peroxide only	< 0.05
Peroxide + molybdate adsorbed on resin	0.55
Peroxide + molybdate	86

The destruction of sulphite and thiosulphate in the "mock" photographic effluent was monitored by observing the pH change with time. The reactions taking place in the mixture are as follows:

$SO_3^{2-} + H_2O_2 \text{ ---> } SO_4^{2-} + H_2O$ Reaction 1

$HSO_3^{-} + H_2O_2 \text{ ---> } SO_4^{2-} + H^+$ Reaction 2

$2S_2O_3^{2-} + H_2O_2 + 2H^+ \text{ ---> } S_4O_6^{2-} + 2H_2O$ Reaction 3

$S_4O_6^{2-} + 7H_2O_2 \text{ ---> } 4SO_4^{2-} + 4H_2O + 6H^+$ Reaction 4

$2H_2O_2 \text{ ---> } 2H_2O + O_2$ Reaction 5

The pH of the mixture starts at around 7. At this pH almost all the sulphite in the mixture will be protonated as the bisulphite and of the first two reactions, reaction 2 will be the more important, so as the reaction takes place the pH should fall as protons are liberated. Reaction 3 must take place before reaction 4. Reaction 3 causes the pH to rise as protons are used and the reaction 4 takes over and the pH falls again. Thus the pH can be used to follow

the reaction. Reaction 5, the peroxide decomposition reaction does not change the pH.

The pH versus time curves for these runs are shown in Figure 1. The initial pH in all runs fell rapidly leaving the thiosulphate to react. The oxidation of thiosulphate in the run containing the resin with molybdate adsorbed was about three time faster than the run without a catalyst. The final pH was also lower suggesting that the reaction had proceeded further. Although the thiosulphate was removed faster and more completely by the run containing the equivalent amount of unadsorbed molybdate, the molybdenum in the effluent was about 150 times greater. This experiment shows that molybdate adsorbed on a resin is an efficient catalyst for the oxidation of photographic effluent with very little molybdenum entering the waste stream.

EXAMPLE 2

Example 1 was repeated with a series of Dowex 1X8 anionic ion-exchange resins. This series has resins of different bead sizes, the last number in the resin's name being the approximate mesh size of the beads, 50 being the largest and 400 the smallest. The 100 mesh beads were found to provide the best catalysis for the reaction, which was surprising as it would have been expected that the smaller bead with the greater surface area would be the most effective.

The resulting pH curves are shown with a control, containing no molybdate, as Figure 2.

Example 3

Example 1 was repeated with two Dowex 1X2 anionic ion-exchange resins, having a different amount of cross-linking compared to the 1X8 series. The resulting pH curves are shown with a control, containing no molybdate, as Figure 3. The reaction rates were similar to those in Example 2, but there was less difference between the 100 and 400 mesh size resins.

Example 4

Example 1 was repeated with a Duolite 6113 resin, a mixed bed resin comprising a mixture of anionic and cationic resins. The resulting pH curves are shown with a control, containing no molybdate, as Figure 4. The mixed bed resin + molybdate showed some increased reaction rate over the control but was not as good as the pure anionic exchange resins.

In practice, the treatment method according to the present invention may be performed batch-wise in a holding tank apparatus (10) as illustrated in Figure 5 or using a continuous feed from a photographic development process, in which case a conduit apparatus (20) of the kind illustrated in Figure 6 may be employed.

The holding tank (17) is equipped with an inlet (11) for receiving photographic effluents batch-wise from a photographic development process. The effluents from the various stages of the process may be treated separately, or may preferably be combined and treated together. The holding tank (17) is also fitted with

an outlet (12) which is provided with a manually operable valve (13). The outlet (12) is arranged for discharging treated effluents from the holding tank (17) to waste, e.g. in a public utility sewage system, via a separator (14) for separating precipitated silver species from the treated effluents.

The holding tank (17) contains a bed (15) of anion exchange resin (16). Alternatively a mixed bed of cation and anion exchange resins may be used. The exchange resin(s) (16) is prior-treated with a solution of a chromate, vanadate or preferably tungstate or molybdate salt as hereinbefore described, so as to immobilise the transition metal oxyanion on the exchange resin(s).

In service, photographic effluents from the development process are introduced batch-wise to the holding tank (17) through inlet (11) with valve (13) in the closed position. If necessary, peroxide, in the form of hydrogen peroxide, or a metal or organic peroxide capable of releasing hydrogen peroxide on contact with water, may be introduced to the holding tank (17) at this stage. Where the treatment is carried out on effluents from an RX development process however, the effluents may themselves already contain sufficient hydrogen peroxide.

The effluents and peroxide are allowed to stand in the holding tank (17) in contact with the ion exchange resin (16) for a predetermined period of time sufficient to allow substantially complete reaction of the hydrogen peroxide with sulphite and thiosulphate anions in the effluents, for example, for a period of

less than 1 hour. This reaction is catalysed by the transition metal oxyanions supported on the exchange resin beads (16), and forms sulphate anions.

The valve (13) is then opened, allowing the effluents to be discharged in the holding tank (17) through the outlet (12). Any precipitated silver species are removed by the separator (14), which may be a filter or centrifuge, and the effluents can then be discharged to waste.

Alternatively, the photographic effluents can be introduced continuously from the photographic development process to the conduit apparatus (20) as shown in Figure 6. In this embodiment, the conduit (27) is generally U-shaped, but different configurations may be employed as desired. The conduit (27) comprises an inlet (21) and an outlet (22) and is packed as shown in Figure 6 with a porous bed of ion exchange resin (26) as previously described. The outlet (22) is equipped with a manually adjustable valve (23) which is operated to control the flow rate of effluents through the conduit (27), such that the average residence time of the effluent in the conduit (27) is sufficient to allow substantially complete destruction of sulphite and thiosulphate to sulphate, for example, preferably less than 1 hour. The effluent is then discharged to waste via a separator (24) as hereinbefore described.

CLAIMS

1. A method of treating waste effluent containing reduced species by oxidation with hydrogen peroxide, or a compound capable of releasing hydrogen peroxide, in the presence of a catalyst therefor, characterised in that said catalyst is immobilised on a substrate therefor.

2. A method as claimed in claim 1 characterised in that the effluent is photographic effluent.

3. A method as claimed in claim 2 characterised in that the effluent is from a process with a redox-amplification developer.

4. A method as claimed in any one of the preceding claims characterised in that the reduced species are sulphur-oxygen species.

5. A method as claimed in claim 4 characterised in that the sulphur-oxygen species are thiosulphate or sulphite.

6. A method of treating waste effluent as claimed in any one of the preceding claims characterised in that the catalyst is selected from molybdate, tungstate, chromate and vanadate.

7. A method as claimed in any one of the preceding claims characterised in that the substrate constitutes a porous mass which permits permeation of the waste effluent into its interstices, thereby presenting a large surface area of catalyst to the effluent.

8. A method as claimed in any one of the preceding claims characterised in that the substrate is an ion exchange material.

9. A method as claimed in claim 8 characterised in that the substrate comprises an anion exchange material.

10. A method as claimed in claim 9 characterised in that the anion exchange material is a Dowex 1X8 - 100 mesh resin.

11. Holding tank apparatus (10) for treating waste effluents, which holding tank apparatus (10) comprises a receptacle (17) containing a catalyst, which catalyst is adapted for catalysing the oxidation of reduced species in waste effluents by hydrogen peroxide, or a compound capable of releasing hydrogen peroxide, and which catalyst is immobilised on a substrate (16) therefor in the receptacle (17), an inlet (11) for introducing effluent from a development process to the receptacle (17), and an outlet (12) fitted with selectively operable closing means (13).

12. Holding tank apparatus (10) as claimed in claim 11 characterised in that the waste effluent is as claimed in any one of claims 2 to 5.

13. Conduit apparatus (20) for treating waste effluents, which conduit apparatus (20) comprises a conduit (27) containing a catalyst, which catalyst is adapted for catalysing the oxidation of reduced species in waste effluents by hydrogen peroxide, or a compound capable of releasing hydrogen peroxide, and which catalyst is immobilised on a substrate (26) therefor, an inlet (21) for introducing waste effluents to the conduit (27), and an outlet (22); whereby in use, waste effluents are supplied continuously to the conduit (27) at a volume throughput to achieve substantially complete oxidation of the reduced species.

14. Conduit apparatus (20) as claimed in claim 13, characterised in that the substrate (26) is porous and is packed in the conduit (27).

15. Conduit apparatus (20) as claimed in claim 13 characterised in that the waste effluent is as claimed in any one of claims 2 to 5.

ABSTRACT

This invention provides a method of treating waste effluent, particularly photographic effluent, containing reduced species such as thiosulphate or sulphite, by oxidation with hydrogen peroxide or a compound capable of releasing hydrogen peroxide, in the presence of a catalyst therefor. The invention is characterised in that the catalyst is immobilised on a substrate. The catalyst may be selected from chromate, vanadate and preferable molybdate or tungstate and the substrate may comprise an ion exchange material, especially an anion exchange material. The invention further provides a holding tank apparatus (10) or a conduit apparatus (20) for carrying out this method.

Figure 1. pH Versus Time Curve for Efflunet Reaction with Peroxide

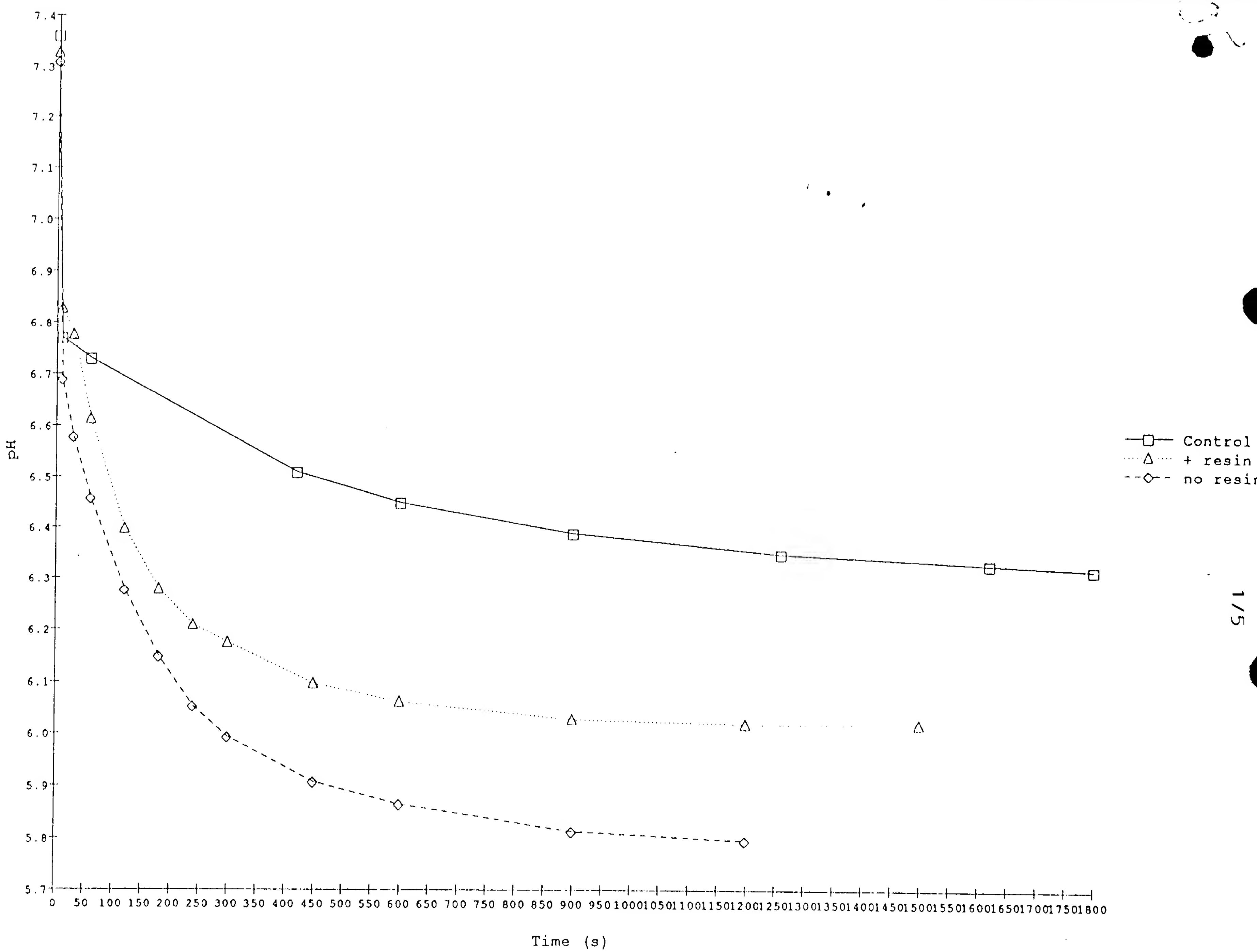

Figure 2. pH versus Time Curve for Effluent Reaction with Peroxide Molybdate + Dowex 1x8 Series Resins

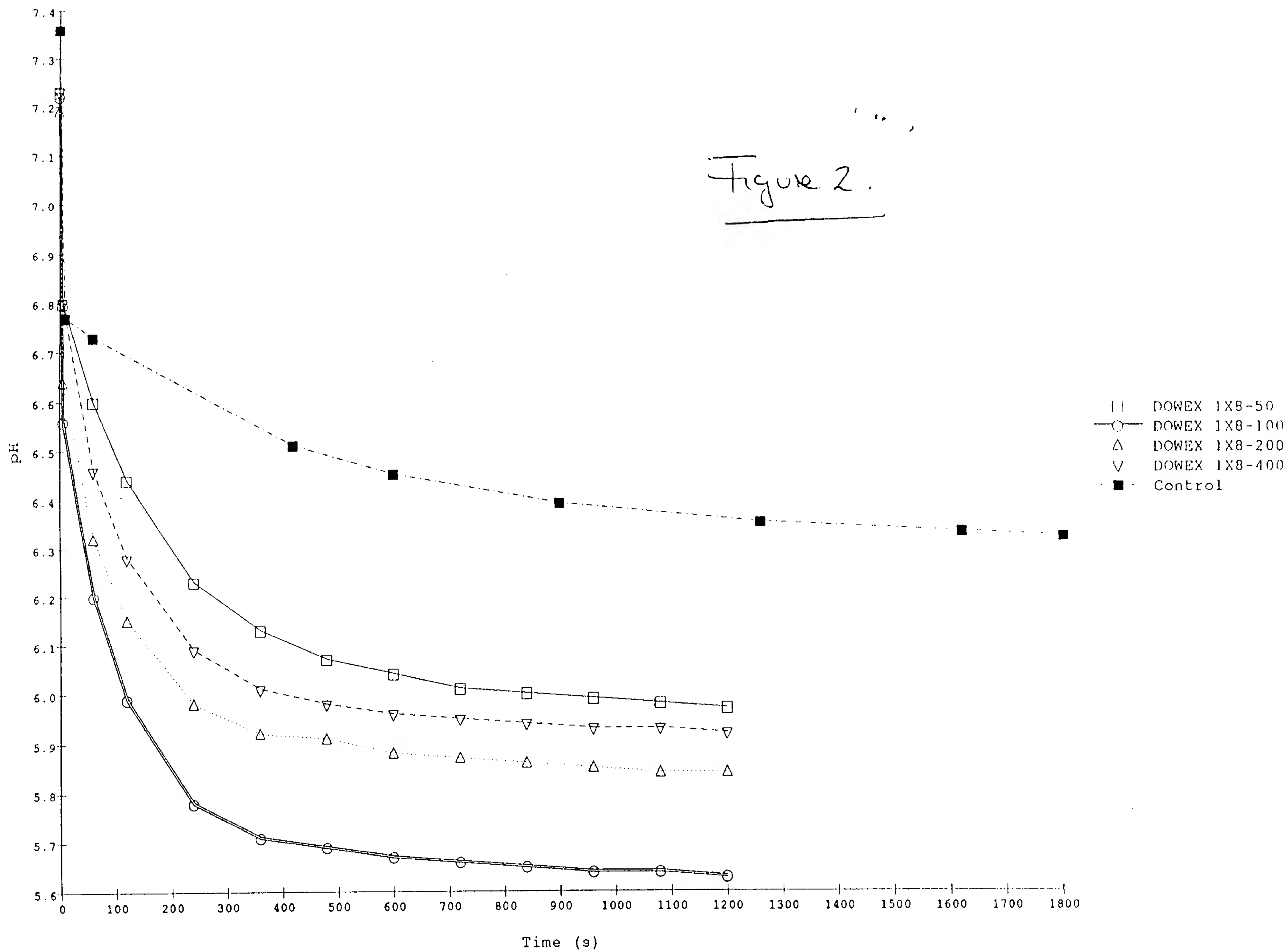

Figure 3. pH versus Time for Effluent Reaction with Peroxide
Molybdate + Dowex 1X2 Series Resins

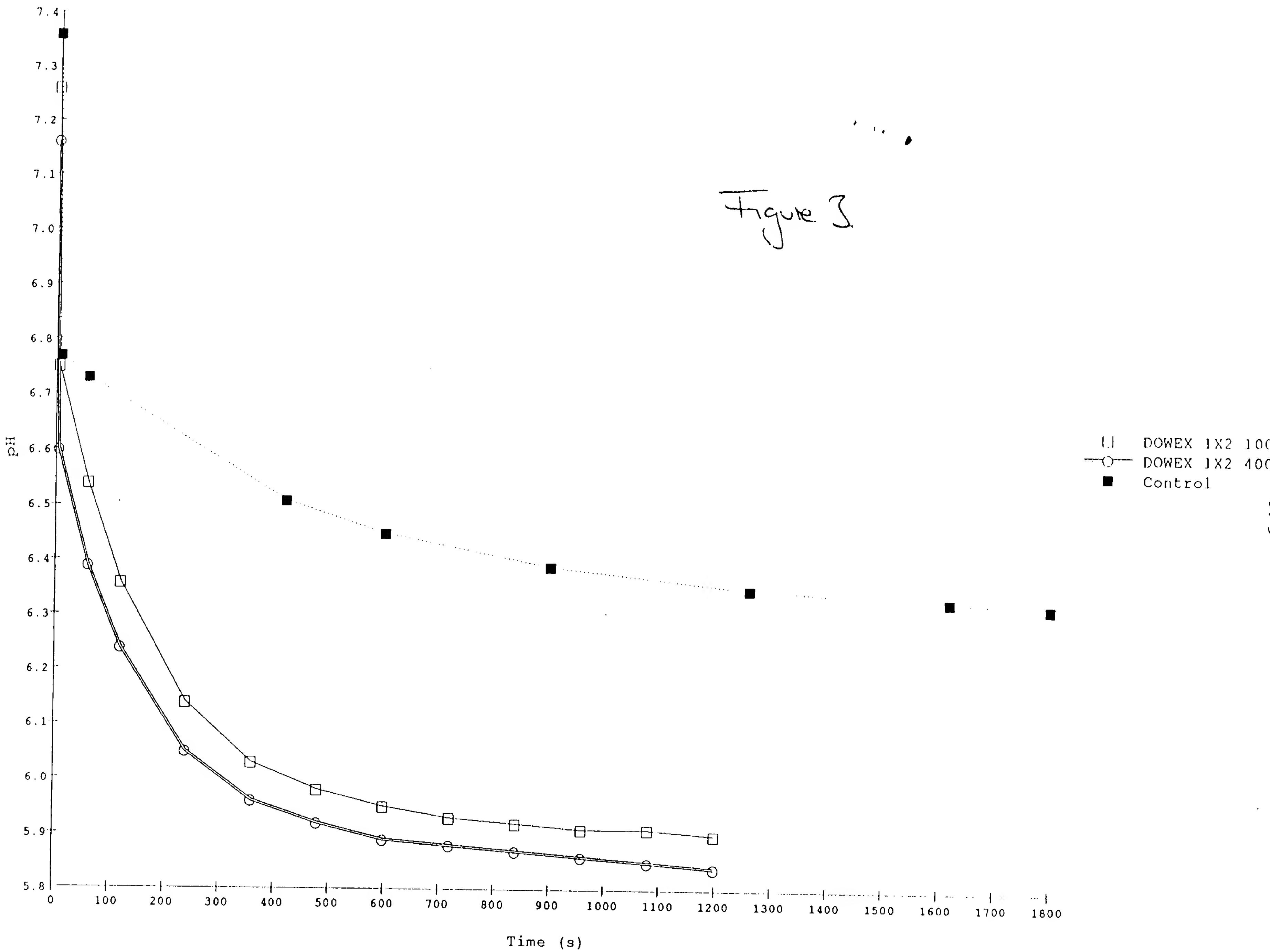

Figure 3

Figure 4. pH versus Time Curve for Effluent Reaction with Peroxide Molybdate + Duolite 6113 Mixed-Bed Resins

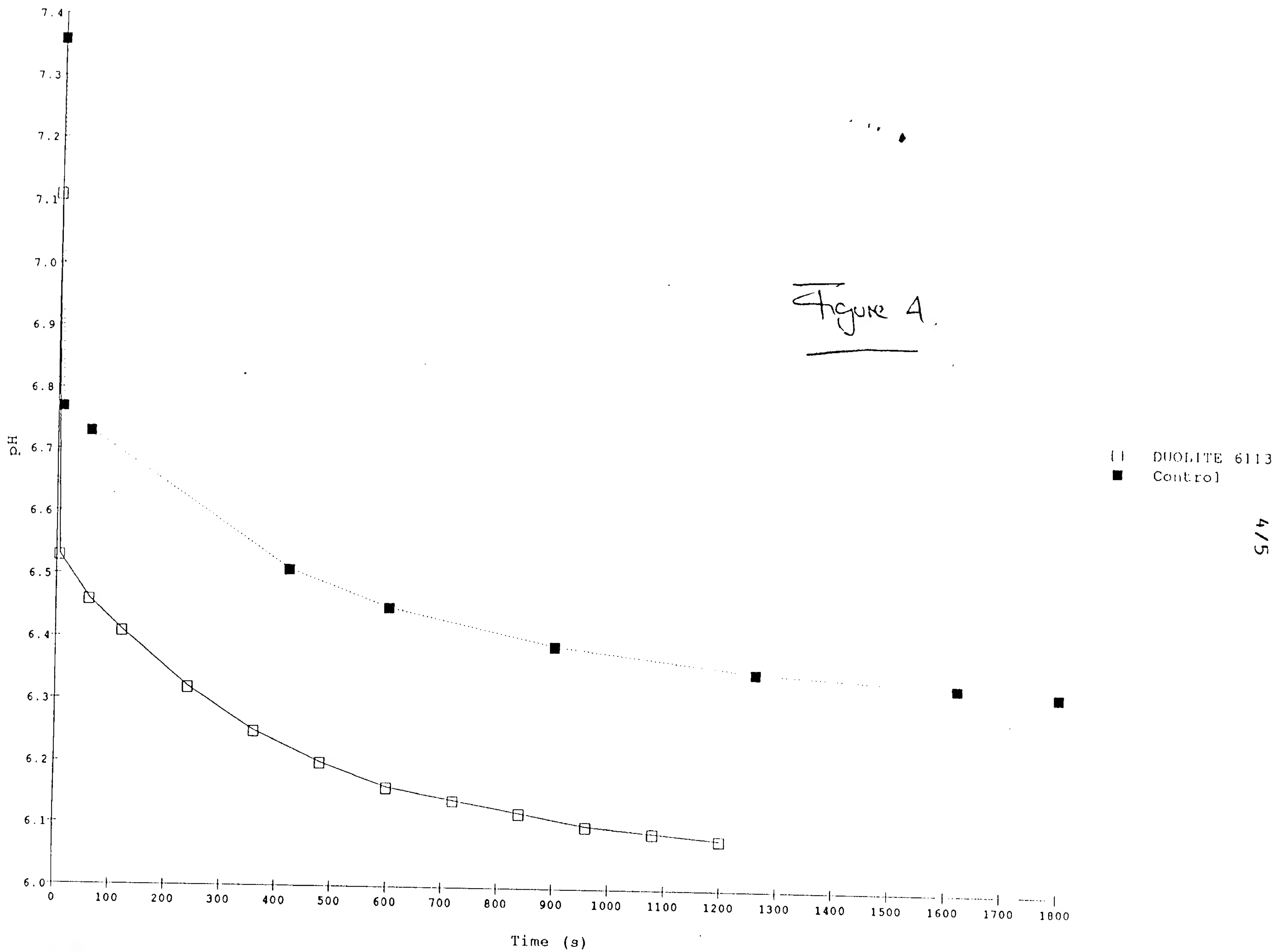

Figure 4

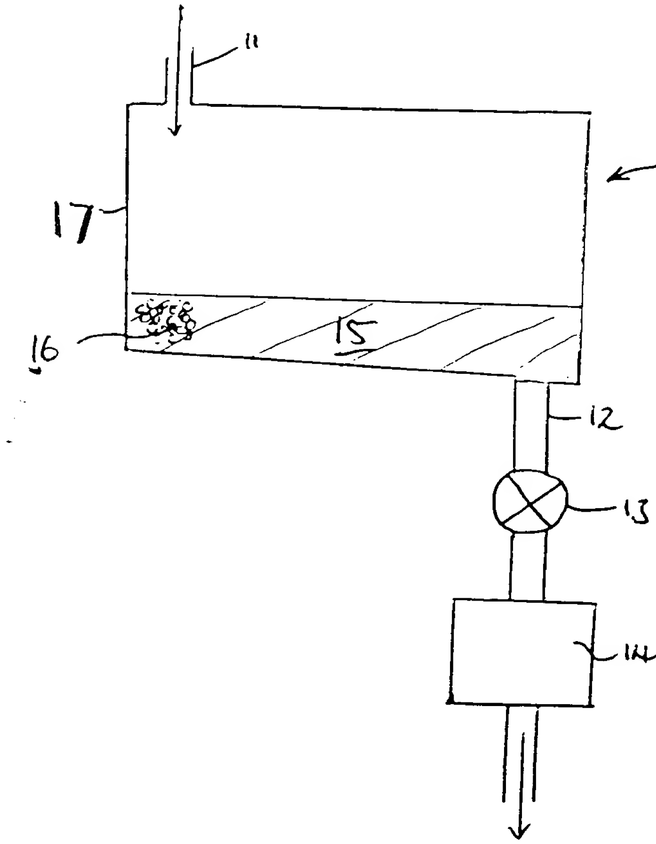

Figure 5

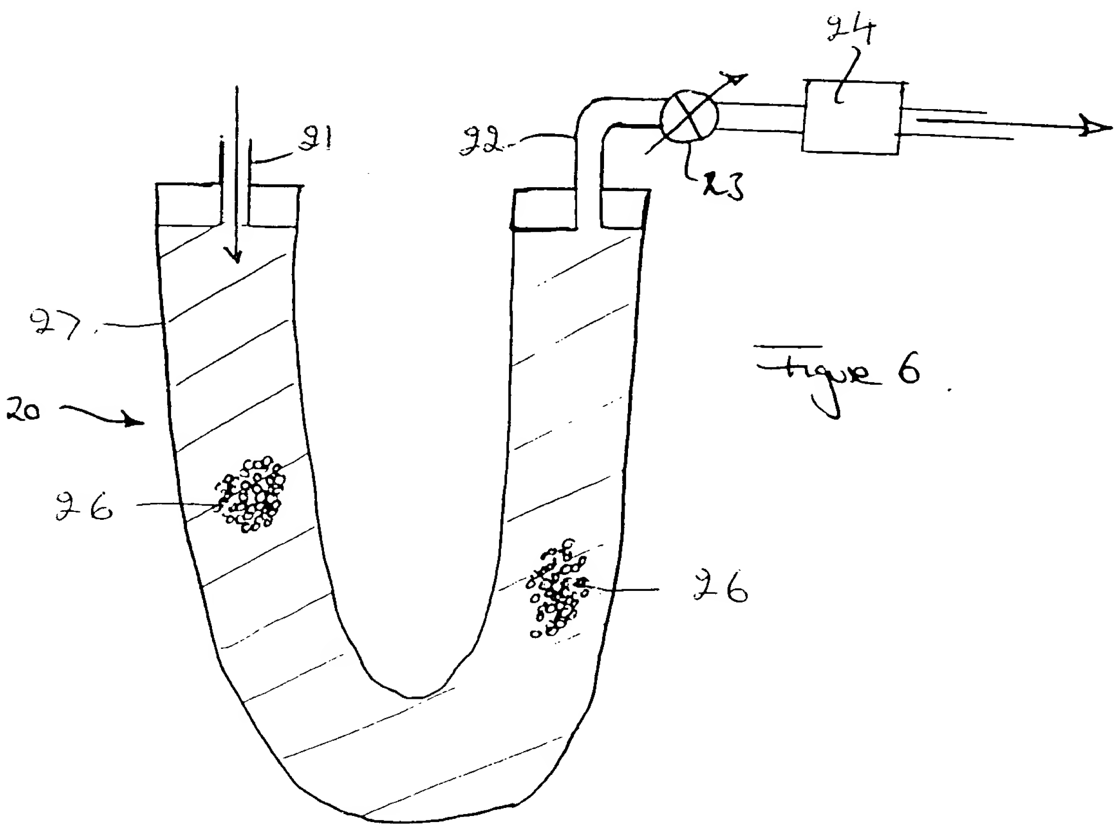

Figure 6